

II.7 RECOMMENDATIONS

This study has indicated the relative magnitude of HAP emissions expected at process drains. However, further research is required to better understand the mechanisms that cause emissions at process drains and to obtain mass transfer coefficients under a greater variety of operating conditions. Recommendations for future work are summarized below:

- A statistical analysis of the data presented in this report is recommended. Confidence intervals for the mass transfer coefficients should be calculated. More experiments may be required to achieve more narrow confidence intervals.
- For experiments in which the HAP emission rates were small (p-trap, no process wastewater flowrate into drain), there was a discrepancy between mass transfer coefficients calculated based on the decline in wastewater concentration ($k_L(L)$) and those calculated using gas samples ($k_L(G)$). This discrepancy should be resolved. Efforts should be made to further reduce miscellaneous leaks and experiments repeated.
- The impact of the location of the drop pipe in the drain on mass transfer coefficients should be investigated. It was postulated that significant emissions resulted from air blowing across the falling liquid, above the drain mouth. The impact of lowering the drop pipe below the drain mouth should be experimentally determined.
- Pilot scale experiments should be conducted under the range of operating conditions likely to be experienced at full scale. These conditions include:
 - sewer pipe length and diameter
 - drain pipe length and diameter
 - length of pipe between drain and p-trap
 - wastewater level in sewer pipe
 - process wastewater and sewer wastewater temperature
 - wind velocities
- Emission data should be collected from full scale operating drains. Flux boxes can be constructed around the drain for the collection of gas samples. The data collected can be compared to pilot scale data and also used for the calibration of mechanistic models.
- A mechanistic model for predicting HAP emissions from process drains should be developed. If complete mechanistic modelling is not possible, semi-empirical models should be derived using the data obtained from the experiments recommended above.

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APPENDIX I.A: DROP STRUCTURE EXPERIMENTAL DATA

Experiment #	1
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	2.7
Drop Height (m)	1.0
Tailwater Depth (m)	0.5
Water Temperature (°C)	24
Headspace Temperature (°C)	20

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	2	3	3	3	3	3
avg concentration (mg/m ³)	69000	34	76	53	68	54
std deviation (mg/m ³)	0	0.5	0.6	1.7	1.1	0.5
DOWNSTREAM LIQUID						
# samples	2	3	3	3	3	3
avg concentration (mg/m ³)	67000	32	72	44	54	41
std deviation (mg/m ³)	1400	0.6	1.1	1.4	1.7	0.9
GAS						
# samples	2	2	2	2	2	2
avg concentration (mg/m ³)	< 36	1.8	4.7	14	14	13
std deviation (mg/m ³)	NA	0.3	0.1	1.0	3.5	0.7
STRIPPING EFFICIENCY (%)						
based on gas	< 0.02	2.1	2.5	10	8.2	9.6
based on liquid difference	3	6	5	17	21	24
KL_a (1/hr)						
based on Equ. 6 (gas)	< 0.016	0.69	0.26	4.3	1.3	1.7
based on Equ. 5 (liquid)	< 2.20	1.9	0.57	7.0	3.2	4.4

Experiment #	2
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	4.0
Drop Height (m)	1.0
Tailwater Depth (m)	0.5
Water Temperature (°C)	28
Headspace Temperature (°C)	23

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	3	3	3	3	3	3
avg concentration (mg/m ³)	19000	264	179	92	96	31
std deviation (mg/m ³)	2000	63	29	9	4	4
DOWNSTREAM LIQUID						
# samples	2	3	3	3	3	3
avg concentration (mg/m ³)	20000	193	159	67	78	25
std deviation (mg/m ³)	0	72	9	8	2	2
GAS						
# samples	2	3	3	3	3	3
avg concentration (mg/m ³)	< 5.2	< 0.3	17	16	34	8
std deviation (mg/m ³)	NA	NA	3	1	2	1
STRIPPING EFFICIENCY (%)						
based on gas	< 0.02	< 0.07	5.6	10	21	15
based on liquid difference	0	27	11	27	19	19
KL_a (1/hr)						
based on Equ. 6 (gas)	< 0.0021	< 0.007	0.77	2.2	4.5	2.3
based on Equ. 5 (liquid)	0	0.052	1.5	6.0	4.0	3.0

Experiment #	3
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	27
Drop Height (m)	1.0
Tailwater Depth (m)	0.5
Water Temperature (°C)	24
Headspace Temperature (°C)	21

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	3	3	3	3	3	3
avg concentration (mg/m ³)	55000	36	76	54	68	54
std deviation (mg/m ³)	8000	3	1	3	3	3
DOWNSTREAM LIQUID						
# samples	2	3	3	3	3	3
avg concentration (mg/m ³)	66000	31	68	38	46	33
std deviation (mg/m ³)	0	0.2	2	0.8	1	1
GAS						
# samples	2	3	3	3	3	3
avg concentration (mg/m ³)	< 39	0.6	1.9	2.8	2.6	3.1
std deviation (mg/m ³)	NA	0.05	1	0.3	0.8	0.5
STRIPPING EFFICIENCY (%)						
based on gas	< 0.3	6.6	9.9	21	15	23
based on liquid difference	0	14	11	30	32	39
KL_a (1/hr)						
based on Equ. 6 (gas)	< 1.2	< 0.80	0.95	2.7	1.9	3.3
based on Equ. 5 (liquid)	0	1.7	1.0	3.9	4.0	5.6

Experiment #	4
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	2.7
Drop Height (m)	0.0
Tailwater Depth (m)	1.3
Water Temperature (°C)	23
Headspace Temperature (°C)	21

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	1	2	2	2	2	2
avg concentration (mg/m ³)	82000	90	86	69	72	63
std deviation (mg/m ³)	NA	1	2	1	2	3
DOWNSTREAM LIQUID						
# samples	1	2	2	2	2	2
avg concentration (mg/m ³)	90000	95	84	68	71	62
std deviation (mg/m ³)	NA	9	8	8	11	9
GAS						
# samples	1	3	3	3	3	3
avg concentration (mg/m ³)	< 10	0.41	0.51	0.44	0.41	0.45
std deviation (mg/m ³)	NA	0.05	0.02	0.03	0.05	0.02
STRIPPING EFFICIENCY (%)						
based on gas	< 0.005	0.2	0.2	0.3	0.2	0.3
based on liquid difference	0	0	2.3	1.4	1.4	1.6
KL_a (1/hr)						
based on Equ. 6 (gas)	<0.0002	0.0054	0.0073	0.0077	0.0068	0.0086
based on Equ. 5 (liquid)	0	0	0.072	0.044	0.042	0.048

Experiment #	5
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	14
Drop Height (m)	0.0
Tailwater Depth (m)	1.3
Water Temperature (°C)	23
Headspace Temperature (°C)	21

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	1	2	2	2	2	2
avg concentration (mg/m ³)	93000	106	97	77	85	76
std deviation (mg/m ³)	NA	1	4	2	5	5
DOWNSTREAM LIQUID						
# samples	1	2	2	2	2	2
avg concentration (mg/m ³)	93000	98	98	74	84	77
std deviation (mg/m ³)	NA	2	4	3	6	5
GAS						
# samples	1	3	3	3	3	3
avg concentration (mg/m ³)	< 10	< 0.06	0.09	0.15	0.11	< 0.06
std deviation (mg/m ³)	NA	NA	0.01	0.04	0.04	NA
STRIPPING EFFICIENCY (%)						
based on gas	< 0.02	0.1	0.2	0.4	0.3	< 0.2
based on liquid difference	0.0	7.5	0	3.9	1.2	0
KL_a (1/hr)						
based on Equ. 6 (gas)	<0.0009	< 0.004	0.0056	0.012	0.0080	< 0.0047
based on Equ. 5 (liquid)	0	0.24	0	0.12	0.035	0

Experiment #	6
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	27
Drop Height (m)	0.0
Tailwater Depth (m)	1.3
Water Temperature (°C)	23
Headspace Temperature (°C)	21

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	0	2	2	2	2	2
avg concentration (mg/m ³)	NA	97	91	70	76	68
std deviation (mg/m ³)	NA	3	2	1	2	3
DOWNSTREAM LIQUID						
# samples	0	3	3	3	3	3
avg concentration (mg/m ³)	NA	99	88	70	75	67
std deviation (mg/m ³)	NA	3	3	2	3	3
GAS						
# samples	0	3	3	3	3	3
avg concentration (mg/m ³)	NA	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07
std deviation (mg/m ³)	NA	NA	NA	NA	NA	NA
STRIPPING EFFICIENCY (%)						
based on gas	NA	< 0.3	< 0.3	< 0.4	< 0.4	< 0.4
based on liquid difference	NA	0	3.3	0	1.3	1.5
KL_a (1/hr)						
based on Equ. 6 (gas)	NA	< 0.008	< 0.0094	< 0.012	< 0.011	< 0.012
based on Equ. 5 (liquid)	NA	0	0.10	0	0.038	0.044

Experiment #	7
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	5.4
Drop Height (m)	0.0
Tailwater Depth (m)	1.1
Water Temperature (°C)	25
Headspace Temperature (°C)	22

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	0	3	2	2	0	2
avg concentration (mg/m ³)	NA	43	41	59	NA	51
std deviation (mg/m ³)	NA	4	1	7	NA	0
DOWNSTREAM LIQUID						
# samples	0	3	3	3	0	3
avg concentration (mg/m ³)	NA	39	29	45	NA	44
std deviation (mg/m ³)	NA	2	5	5	MA	4
GAS						
# samples	0	3	3	3	3	3
avg concentration (mg/m ³)	NA	0.78	0.98	1.7	NA	1.3
std deviation (mg/m ³)	NA	0.01	0.2	0.2	NA	0.09
STRIPPING EFFICIENCY (%)						
based on gas	NA	1.4	1.9	2.3	NA	2.0
based on liquid difference	NA	9.3	29	24	NA	14
KL_a (1/hr)						
based on Equ. 6 (gas)	NA	0.075	0.11	0.12	NA	0.085
based on Equ. 5 (liquid)	NA	0.49	1.7	1.2	NA	0.58

Experiment #	8
Water Flowrate (m ³ /h)	6.8
Gas Flowrate (m ³ /h)	27
Drop Height (m)	0.0
Tailwater Depth (m)	1.1
Water Temperature (°C)	25
Headspace Temperature (°C)	22

	METH	DCB	TOL	TCE	TCA	PERC
UPSTREAM LIQUID						
# samples	0	3	3	3	0	3
avg concentration (mg/m ³)	NA	48	32	51	NA	41
std deviation (mg/m ³)	NA	1	2	2	NA	3
DOWNSTREAM LIQUID						
# samples	0	3	2	2	0	2
avg concentration (mg/m ³)	NA	42	30	44	NA	43
std deviation (mg/m ³)	NA	6	2	3	MA	3
GAS						
# samples	0	3	3	3	0	3
avg concentration (mg/m ³)	NA	0.15	0.21	9.25	NA	0.22
std deviation (mg/m ³)	NA	0.01	0.02	0.02	NA	0.02
STRIPPING EFFICIENCY (%)						
based on gas	NA	1.2	2.6	2.0	NA	2.1
based on liquid difference	NA	13	6	14	NA	0
KL_a (1/hr)						
based on Equ. 6 (gas)	NA	0.052	0.10	0.08	NA	0.071
based on Equ. 5 (liquid)	NA	0.52	0.24	0.56	NA	0

APPENDIX II-A
ANALYTICAL METHODS

VOCs in Wastewater:

EPA 1625- Revision C: Code of Federal Regulations, June 1989

VOCs in Air:

EPA TO-14:

Compendium of Methods For The Determination of Toxic Organic Compounds in Ambient Air; EPA/600/4-89/017, June 1988

Methanol in Wastewater:

direct aqueous injection: injection volume 1 uL
DBWAX column; 32 mm Diameter; 30 m Length
FID detector

Methanol in Air:

NIOSH 2000: NIOSH Manual of Analytical Methods, 3rd Edition (1984)

APPENDIX Q

APPENDIX Q

**COMMENTS ON PROPOSED METHODS 21, 304 AND 305
CONTAINED IN THE HAZARDOUS ORGANIC NESHAP**

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ENVIRΩMEGA

EXECUTIVE SUMMARY

The enclosed report presents comments regarding proposed Methods 21, 304 and 305 in the proposed wastewater provisions of the Hazardous Organic NESHAP (HON) for the synthetic organic chemical manufacturing industry.

Method 21:

In general wastewater vessels that receive, manage or treat a group 1 wastewater will be required to operate and maintain one of the following control devices:

- fixed roof and closed vent system
- fixed roof and internal floating roof
- external floating roof

For internal and external floating roof tanks, compliance is demonstrated by physical inspection of the floating roof seal on a periodic basis. For fixed roof tanks, compliance is demonstrated by assuring that the fixed roof and all openings are operated without leaks as indicated by an instrument reading of less than 500 ppmV above background, as determined by EPA Method 21.

Method 21 was developed for detecting leaks from process equipment at action levels of 10,000 ppmV. The 500 ppmV leak definition found in Subpart G of the HON appears to be derived from leak definitions for equipment leaks. The affected components of wastewater vessels include mechanically installed or operated components such as hatches and access doors. The types of components are all covered in the current version of Method 21 for process components. It is assumed that the tank surface and welded seams are not affected. It is also assumed, but not stated in Subpart G, that the two conditions described in Subpart H as "unsafe to screen" and "inaccessible" will also apply to Subpart G affected components.

There is inconsistency in the definition of a group 1 vessel between the storage vessel provisions and the wastewater provisions. In the wastewater provisions, a group 1 vessel is any vessel that receives a group 1 wastewater. In the storage vessel provisions, the definition of a group 1 vessel is dependent on the total partial pressure of HAPs contained in the vessel. In many cases, application of the wastewater definitions will require control of vessels with a relatively low HAP partial pressure and low potential for significant leaks. In addition, application of method 21 would be futile since the vapor content within the tank itself may be less than the 500 ppmV leak definition.

Within Subpart G, it is specified that the method 21 calibration gas will be a mixture of methane in air. This restriction precludes the use of several reference gases for which response factors of the affected VOHAP have been determined and limits the use of instruments to those with FID or NDIR detectors. Method 21 was originally intended for the detection of leaks from components containing pure compounds or mixtures of a relatively small number of HAPs. Wastewater matrices are likely to be more complex. Within Subpart

G it is stated to use the predominant VOHAP in the wastewater stream to determine the Method 21 response factor. Screening values would be biased high in the case where a secondary VOHAP has a higher response factor than the predominant VOHAP.

Method 304:

Many of the HAPs considered in the HON are readily biodegradable and biological treatment is potentially a very effective method of treatment. Within the HON, it is stated that biological wastewater treatment may be used to comply with the HON although they must achieve a comparable control efficiency as the reference control technology (steam stripper). To demonstrate compliance, the EPA developed model, WATER7, must be used with biokinetic constants determined using Method 304. It was not clearly stated under what conditions Method 304 will be required.

WATER7 is one of many models available for predicting the fate of organic compounds in biological wastewater treatment plants. All these models address the three potential removal mechanisms within a plant:

- stripping and volatilization
- sorption and removal with waste sludge
- biodegradation

Within a given system, the three removal mechanisms are independent although they compete with each other. If the rate of biodegradation is very rapid, the total removed by the other two mechanisms will be small. The rates of removal by volatilization/stripping and sorption onto waste activated sludge can be quantified to a reasonable degree of accuracy because they are based on physical-chemical characteristics and mechanisms that are reasonably well understood. Many environmental factors may influence the biodegradation rate of a specific contaminant, possibly causing the biodegradation rate to change with time. However, general tendencies for a compound to biodegrade are a function of chemical characteristics allowing for the use of biodegradation kinetic constants from data-bases to be used as starting points for estimating biodegradation rates. Many techniques have been used for the measurement of biodegradation rates, although a standard method that addresses all applications has not been accepted.

For regulatory purposes, the individual models must be configured to represent physical characteristics of the treatment plant. Secondly, the physical-chemical characteristics of the compounds of interest must be input for predicting removal by stripping/volatilization and sorption. Finally, the biodegradation rate coefficient for the individual compound must be input the model. Method 304 is proposed for obtaining site-specific biodegradation rate coefficients. In method 304, an air tight bench top bioreactor is operated to simulate full scale operating conditions. Air, supplemented with oxygen is continuously re-circulated minimizing stripping/volatilization losses. The rate of biodegradation of a specific HAP is calculated by the difference between the influent and effluent sample concentrations.

Fundamentally, Method 304 is valid for determining first order biodegradation rate coefficients. However, multiple experiments will be required to determine the appropriate Monod kinetic constants utilized by WATER7. In addition the method is complex and potentially expensive to complete.

A number of specific concerns with reactor design were identified including:

- mixing within the aeration tank
- potential build-up of potential inhibitory compounds
- inadequate tubing specification for VOCs
- potential for severe foaming in bench scale reactor
- growth of biomass on reactor walls and instruments
- potential pressure build up in reactor during test
- use of immersion heater in an oxygen environment is a safety hazard
- difficulty in controlling DO to required levels
- inadequate guidance regarding explosion hazard procedures
- equipment is not commercially available

A number of concerns with system operation were also identified:

- sorption of stored wastewater to polyethylene containers
- use of MLSS control rather than SRT control
- requirement to vent headspace to allow for control of DO and pressure both
- flow variability requirement of < 5%
- inadequate definition of steady state conditions
- potential need for defoamers not required in full scale system
- high variability in HAP concentration from an influent flow taken from an equalization tank
- assumption that measured effluent concentration equals dissolved concentration
- potential requirement to acclimate biomass

A number of concerns with sampling and analysis were also identified:

- inability to satisfy 15% relative standard deviation for wastewater samples
- potential requirement for multiple sample analysis requiring substantial sample volume

Given the large number of concerns identified above, an alternative open, bench scale approach may be warranted. In this method, the concentrations of HAPs contained in the offgas are measured and quantified as a mass flux. The method has the disadvantage that a number of gas phase sampling procedures may be required to quantify the off-gas emissions.

Two alternative approaches for compliance demonstration are presented in which the contaminant behaviour in the full scale plant is employed along with a model to estimate the fraction of contaminants biodegraded. For these methods, an accurate model of the stripping/volatilization and sorption losses is required to determine the biodegradation rate.

However, accurate models will be required to demonstrate compliance, even if Method 304 is used to determine the biodegradation rate coefficients. The approaches presented have been employed successfully to aid in obtaining permission for a POTW expansion at the Seattle, Renton plant.

Method 305:

The classification of a wastewater stream as either group 1 (requiring control) or group 2 (not requiring control) is dependent on the flowrate of the stream and the volatile organic HAP (VOHAP) concentration. VOHAP is defined as the volatile portion of an individually-specified organic HAP in a wastewater stream measured by proposed Method 305. As an alternative, total volatile organic (VO) average concentration may be measured as a surrogate for total VOHAP concentration using Method 25D of CFR Part 60. As a second alternative, operators may measure organic HAP concentrations in the wastewater using an approved method and correct the concentration using fraction measured (F_m) factors presented in the HON.

Method 305 is a combination of method 25D for the measurement of total VO in wastewater and method 18 for speciation of individual HAPs. The sampling and purging conditions in method 305 are identical to those in 25D. Samples are collected from sample taps on the wastewater stream lines into vials containing chilled polyethylene glycol. Once in the laboratory the sample is mixed with a polyethylene glycol mixture and purged for 6 hours at a flowrate of 6 L/min and temperature of 75 °C. However, rather than using a continuous detector, the purge gas is collected on sorbent tubes and the individual HAPs quantitatively speciated. Total VOHAP concentration is determined by summing the mass of all the HAPs collected on the sorbent tube and dividing the sum by the wastewater sample volume.

The elevated purging temperature and purging length do not represent stripping/volatilization conditions generally encountered in wastewater collection and treatment. Thus, the classification of a wastewater as either group 1 or group 2 based on method 305 is based on an arbitrary measurement of concentration. Since the measurement is arbitrary, direct sampling and measurement of the contaminants in the wastewater stream using established EPA methods is preferred to the complex methods proposed. At the present time, the equipment required for Method 305 is not commercially available potentially delaying the implementation of the HON. If a gas phase measurement is required, headspace GC, in which equilibrium between the liquid and gas phase is achieved, is a potentially simpler alternative.

There are a number of concerns with sorbent tube selection and capacity. No one sorbent tube is applicable to all HAPs. Wastewater streams that contain different classes of organics will likely require multiple purge sequences increasing operational and analytical costs of the method. The total purge volume exceeds the limit for many sorbents such as Tenax. The level of organics in wastewater streams, at their regulatory limit, precludes the use of thermal desorption for analysis. Solvent extraction has been associated with poorer precision and accuracy than thermal desorption for some of the regulated organics. It may

be difficult or impossible to quantify the concentration of low concentration HAPs, because of the presence of high concentration volatiles (not necessarily HAPs) to comply with the required regulations for new sources (Subpart G, Table 8 compounds).

Two measures of trapping efficiency of the purge stream and recovery of the analytes are required in Method 305. However, only one of these is presented in the December 31, 1992 version of method 305 presented in the Federal Register, although provision is made for its use in the final calculations. The reported VOHAP mass is corrected for both these factors although they both measure losses through sorbent desorption and analysis. Thus, by adjusting results based on the product of the two factors, samples will be adjusted twice for the same effects.

Method 305 specifies a recovery efficiency ranging between 50% to 130% must be obtained to ensure that a sorbent tube is appropriate for the compounds of interest. Typical sorbent methods (e.g. NIOSH Method 18) require much more stringent demonstration of precision. The minimum acceptable recovery efficiency of 50% appears arbitrary with no statistical foundation.

Method 305 requires specifies analysis of three calibration standards in triplicate on a daily basis, with all response factors within 5% of the mean of three response factors determined at separate concentrations. The consequence of such stringent calibration requirements is that the number of samples that can be analyzed per day may be quite small.

An interlaboratory study of Method 25D indicated significant laboratory bias relative to theoretical values for the limited number of compounds studied. Each laboratory was supplied with the required apparatus, because it is not commercially available, and detailed instructions. Potential operating concerns, such as cleaning of glassware and the coalescing filter have also been identified.

It is highly likely that many SOCMF facilities will elect to use traditional wastewater analysis data and correct results with fraction measured values provided in the Table 13 of Subpart G of the HON for 84 compounds. These factors generally indicate 100% conversion for many of the non-polar, non water soluble compounds. The means of determination of the F_m factors is not presented in the HON, nor have the values been widely reported in the open literature. The data for certain compounds, such as phosgene, leads to concerns about data validity. There should be full and verifiable documentation of the procedures used and the results obtained by the EPA during the method development and ample time for peer review and open literature publication. The means of determination should be fully validated before factors are set in the HON.

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1. INTRODUCTION

The Environmental Protection Agency (EPA) is proposing to regulate the emissions of certain organic hazardous air pollutants (HAPs) from synthetic organic chemical manufacturing industry (SOCMI) production processes which are part of major sources under Section 112 of the Clean Air Act as amended in 1990. The proposed rule, referred to as the hazardous organic NESHAP (HON), will require sources to achieve maximum achievable control technology consistent with Section 112(d) of the Act. The proposed rule will require control of emissions of 149 of the organic chemicals identified in the Act's list of 189 HAPs at both new and existing SOCMI sources. Source applicability is presented in the Code of Federal Regulations (CFR) Part 63 Subpart F.

The HON rules will cover emission source types that are common to SOCMI member production processes. The required control for the following source types are presented in CFR Part 63 Subpart G:

- process vents
- storage tanks
- chemical transfer operations
- wastewater handling and treatment

The required controls for equipment leaks are presented in Subpart H. The provisions presented in Subpart H would apply to all 149 organic HAPs. The provisions presented in Subpart G would apply only to 112 of these organic HAPs that the EPA has determined may be emitted from SOCMI processes because they are produced as a product or used as a reactant.

1.1 TASKS

Enviromega was contracted by the Chemical Manufacturers Association (CMA) to comment on specific test methods 21, 304 and 305 in the proposed wastewater provisions of the HON. These comments are presented in this report.

2. HON WASTEWATER PROVISIONS

2.1 WASTEWATER CLASSIFICATION

In the proposed HON, wastewater streams are categorized as either group 1 or group 2. Group 1 wastewaters require control while group 2 wastewater require no control. A group 1 wastewater is defined in the proposed HON rule as a wastewater stream meeting any of the criteria presented below:

1. A wastewater stream from a process unit at a new or existing source with a total volatile organic hazardous air pollutant (VOHAP) average concentration greater than or equal to 10,000 ppm or 1% by weight of compounds listed in Table 9 of 63.131 of Subpart G.
2. A wastewater stream from a process unit at a new or existing source that has an average flow rate greater than 10 liters per minute and a total VOHAP average concentration equal to or greater than 1000 ppm by weight of compounds listed in Table 9 of 63.131 of Subpart G.
3. A process wastewater stream at a new source that has a flow rate of 0.02 liters per minute and an average concentration greater than 10 ppm by weight of any compounds listed in Table 8 of 63:131 of Subpart G.

A group 2 wastewater stream is defined as any process wastewater stream that does not meet the definition of a group 1 wastewater stream as defined above. Average flow rate and total VOHAP average concentration are determined for the point of generation of each process wastewater stream.

VOHAP is defined as the volatile portion of an individually-speciated organic HAP in a wastewater stream or a residual that is measured by proposed Method 305. As an alternative, total volatile organic (VO) average concentration may be measured as a surrogate for total VOHAP concentration using Method 25D of CFR Part 60, Appendix A. As a second alternative, operators may measure organic HAP concentrations in the wastewater using a method validated according to Section 5.1 or 5.3 of Method 301 of Appendix A 40 CFR Part 63. The concentrations of the individual organic HAP compounds measured in the water may be corrected to their concentrations had they been measured by proposed Method 305, by multiplying each concentration by the compound-specific fraction measured (F_m) factor in Table 13 Subpart G.

2.2 WASTEWATER TRANSPORT AND STORAGE

The components which receive, manage or treat a group 1 wastewater stream or a residual removed from the wastewater stream, which are affected by the proposed HON rule include the following:

- Wastewater Tanks

- Surface Impoundments
- Containers
- Individual Drain Systems
- Oil-Water Separators

Each wastewater tank that receives, manages, or treats a group 1 wastewater stream or a residual removed from a group 1 wastewater stream shall operate and maintain one of the following control devices:

1. A fixed roof and a closed vent system that routes the VOHAP vapors from the wastewater tank to a control device.
2. A fixed roof and an internal floating roof that comply with the provisions specified in Section 63.119(b) of Subpart G.
3. An external floating roof that meets the requirements specified in Sections 63.119(c), 63.120(b)(5) and 63.120(b)(6) of Subpart G.

For internal and external floating roof tanks, compliance is demonstrated by physical inspections of the floating roof seal on a periodic basis. For fixed roof tanks, compliance is demonstrated by assuring that the fixed roof and all openings (e.g. access hatches, sampling ports, and gauge wells) are operated without leaks as indicated by an instrument reading of less than 500 ppmv above background, as determined by EPA Method 21. EPA Method 21 is conducted initially and then annually thereafter.

Each surface impoundment that receives, manages, or treats a group 1 wastewater stream or a residual removed from a group 1 wastewater stream shall operate and maintain a cover (air-supported structure or rigid cover) and a closed vent system that routes the VOHAP vapors from the surface impoundment to a control device. Compliance is demonstrated by assuring that the cover and all openings (e.g. access hatches, sampling ports, and gauge wells) are operated without leaks as indicated by an instrument reading of less than 500 ppmv above background, as determined by EPA Method 21. EPA Method 21 is conducted initially and then annually thereafter.

Each container that receives, manages, or treats a group 1 wastewater stream or a residual removed from a group 1 wastewater stream shall maintain a cover on each container that is used to handle, transfer or store a Group 1 wastewater stream or a residual removed from a group 1 wastewater stream. Whenever it is necessary to open a container, or whenever aeration, thermal or other treatment of a Group 1 wastewater or residual is necessary in a container, the container shall be located within an enclosure with a closed vent system that routes the VOHAP vapors from the enclosure to a control device. Compliance is demonstrated by assuring that the cover, the enclosure, and all openings (e.g. bungs, hatches, doors, sampling ports, and pressure relief devices) are operated without leaks as indicated by an instrument reading of less than 500 ppmv above background, as determined by EPA Method 21. EPA Method 21 is conducted initially and then annually thereafter.

Each individual drain system, not equipped with a water seal-type trap, that receives, manages, or treats a Group 1 wastewater stream or a residual removed from a group 1 wastewater stream shall operate and maintain a cover and a closed vent system that routes the VOHAP vapors from the individual drain system to a control device. Compliance is demonstrated by assuring that the cover and all openings (e.g. hatches, sampling ports, etc.) are operated without leaks as indicated by an instrument reading of less than 500 ppmv above background, as determined by EPA Method 21. EPA Method 21 is conducted initially and then annually thereafter.

Each oil-water separator that receives, manages, or treats a Group 1 wastewater stream or a residual removed from a group 1 wastewater stream shall operate and maintain one of the following control devices:

1. A fixed roof and a closed vent system that routes the VOHAP vapors from the oil-water separator to a control device.
2. A floating roof which meets the requirements of 40 CFR 60.693-2, and, for portions of the oil-water separator where it is infeasible to construct and operate a floating roof, such as over the weir mechanism, a fixed roof and a closed vent system that routes the VOHAP vapors from the oil-water separator to a control device.

For fixed roof applications in oil-water separators, compliance is demonstrated by assuring that the fixed roof and all openings (e.g. access hatches, sampling ports, and gauge wells) are operated without leaks as indicated by an instrument reading of less than 500 ppmv above background, as determined by EPA Method 21. EPA Method 21 is conducted initially and then annually thereafter.

2.3 CONTROL TECHNOLOGIES

The proposed HON wastewater provisions have identified steam stripping as the reference control technology. The EPA has identified the resulting control efficiency achieved through the application of the reference control technology based upon the physical-chemical properties of the HAPs. Three strippability groups A, B and C were formed (Subpart G, Table 9). The removal efficiency for each strippability group is:

- Strippability Group A: 99%
- Strippability Group B: 95%
- Strippability Group C: 70%

At present, the industry standard for wastewater treatment is biological treatment, perhaps with enhanced physical chemical treatment, such as the addition of activated carbon. While biological treatment units and other technologies may be used to comply with the HON, they must achieve a comparable control efficiency as the reference control technology. However, a model of the biological treatment process is required to demonstrate control efficiency because of the competing removal mechanisms of stripping and volatilization. At present the EPA developed model WATER7 is the only proposed model. The equation

presented for the calculation of mass removal from a biological treatment unit is summarized as:

$$MR = [E_b - E_a] * F_{bio}$$

where:

MR = Actual mass removal by the treatment process or series of treatment processes of total VOHAP for Table 9 HAP compounds or VOHAP from Table 8 compounds [kg per hour].

E_b = Mass flowrate of total VOHAP for Table 9 HAP compounds or VOHAP from Table 8 compounds entering the treatment process or series of treatment processes [kg per hour].

E_a = Mass flowrate of total VOHAP for Table 9 HAP compounds or VOHAP from Table 8 compounds exiting the treatment process or series of treatment processes [kg per hour].

F_{bio} = The fraction of VOHAP from Table 8 HAP compounds, or total VOHAP for Table 9 compounds biodegraded in a properly operated biological treatment unit. The fraction shall be determined using WATER7. The site specific biorate constants used as inputs to WATER7 shall be determined using Method 304 of Appendix A.

The EPA has proposed Method 304 for the determination of site specific bio-kinetic rate constants for use in WATER7. Appropriate biological treatment unit operating parameters must be monitored and reported on a monthly basis for continuous compliance demonstration. The operator must obtain approval for the selection of these appropriate parameters from the EPA Administrator in accordance with 63.143(c).

There is substantial discussion in the Preamble to Part 63 regarding the use of biological treatment as a control technology. The EPA is considering the use of a well operated and maintained biological treatment unit, in conjunction with trapped individual drain systems, as a reference control technology for biodegradable HAPs. In addition, while the EPA has proposed the use of the model WATER7 for demonstrating biological treatment unit performance, they are considering the use of other models such as PAVE, BASTE and TOXCHEM. The EPA is also considering alternatives to Method 304 for the selection of bio-kinetic rate constants for input into the predictive model. In the preamble, it is stated that if models are used without Method 304 inputs, the model parameters would be required to match the biological treatment unit's operating parameters, such as effluent concentration. If the two sets of parameters are not consistent, the operator would be required to re-establish parameter ranges and derive the biodegradation rate by running Method 304.

In response to a question of what triggers the need to perform Method 304 to demonstrate compliance, the EPA responded in the Preamble to Part 63 that an initial

demonstration is required. In addition, Method 304 may be required to be run after the initial demonstration under these conditions:

- (1) addition of a new process unit to the source or after a change in the characteristics of an existing process,
- (2) scheduled checks at least once every five years,
- (3) whenever a performance test is required (e.g. changes in established parameters or operation of the biological treatment unit)

3. DISCUSSION OF PROPOSED METHOD 21

3.1 METHOD PRINCIPLE

Method 21 was developed as a method for the determination of volatile organic compound leaks from process equipment. The procedures described in the method are only intended to locate and classify leaks, not to measure mass emission rates from individual sources. Process equipment components in the chemical industry for which the method was developed include, but are not limited to the following:

1. valves
2. flanges
3. pumps
4. compressors
5. pressure relief devices
6. process drains
7. open-ended valves
8. pump and compressor seal system degassing vents
9. accumulator vessel vents
10. agitator seals
11. access door seals

A portable instrument is used to detect VOC leaks from individual components. The detector type is not specified, but must meet the following criteria:

1. The detector must respond to the compound(s) handled by the affected component(s). The response time must be ≤ 30 seconds, the response factor of the compound in relation to the reference calibration gas must be known, and the response factor must be less than 10.
2. The instrument range and the calibration range of the instrument must encompass the leak definition concentration.
3. The scale of the instrument meter must be readable to $\pm 2.5\%$ of the leak definition concentration.
4. The instrument must be equipped with an electrically driven pump to ensure that the sample is delivered to the detector at a constant flow rate.
5. The instrument must be intrinsically safe if operated in a potentially explosive atmosphere.
6. The instrument must be equipped with a sample probe with a maximum diameter of "

The general operational procedure of method 21, as it applies to a leak definition based upon

concentration, is as follows:

1. Calibrate the selected instrument as described in the Method.
2. Place the probe inlet at the surface of the component interface where leakage could occur.
3. Move the probe along the interface periphery while observing the instrument readout.
4. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum reading is obtained.
5. Leave the probe inlet at this maximum reading location for approximately 2 times the instrument response time, note the maximum reading obtained.
6. Immediately allow the instrument to sample the ambient air in the immediate vicinity of the component not affected by the component (background) for approximately 2 times the instrument response time.
7. Subtract the background reading determined in step 6 from the maximum screening value determined in step 5.
8. If the maximum observed meter reading minus background is greater than the leak definition in the applicable regulation, record and report the results as specified.

3.2 LEAK DEFINITION

Method 21 was originally intended to evaluate leaks of pure compounds from process components at action or leak rate levels of 10,000 ppmv. The 500 ppmv leak definition found in Subpart G of the HON appears to have been derived from leak definitions for equipment leaks. A discussion of this subject is found in Section VII of the HON, "Rationale for Provisions in Subpart H", Subsection C., "Background Information on Equipment Leaks", beginning on page 62660. In the 1980's, EPA sponsored studies which measured emission rates from various types of equipment (e.g. valves, flanges, pumps, etc.) and corresponding screening values based on method 21. Although the results of these studies varied widely, it was determined that by implementing an inspection and maintenance program in which equipment leaks over 10,000 ppmV as determined by Method 21 were limited and repaired, a 60 to 70 percent reduction in fugitive emissions would occur. In order to achieve MACT under the HON, various leak definitions of 500 to 2,000 ppmV were considered to demonstrate further fugitive emission reductions. Ultimately, a leak definition of 500 ppmV was selected in light of demonstrating that the ability to measure and repair small leaks less than 500 ppmV was not practical. This leak definition was then adopted for the wastewater provisions under Subpart G.

In 1990 a study, funded by EPA, was published evaluating the applicability of method 21 for the VOHAP chemicals regulated under the HON at the 500 ppmv level.¹ This study

determined response factors for these chemicals at the 500 ppmv level for portable flame ionization detectors (FIDs), photo ionization detectors (PIDs), and non-dispersive infrared (NDIR) detectors. The study concluded that, in general, the applicability of the measurement accuracy remains somewhat compound dependent, but overall the use of one or more of the above detector types for most of the VOHAP compounds is acceptable at the 500 ppmv level.

The 500 ppmv leak definition is also qualified to be "500 parts per million by volume above background". Each time a component is leak checked by method 21, a simultaneous background reading is also obtained. Any detected background reading is subtracted from the maximum screening value of the component before a leak determination is made. This procedure will eliminate any interference from background VOC concentrations which may bias a method 21 leak measurement.

3.3 CONCERNS WITH THE APPLICATION OF METHOD 21

3.3.1 WASTEWATER COMPONENTS REQUIRING LEAK DETECTION

The affected components of wastewater tanks, surface impoundments, containers, individual drain systems, and oil water separators which must be operated without leaks as determined by application of method 21 include hatches, access doors, sampling ports, pressure relief devices, gauge wells, etc. These types of components are all covered in the current version of Method 21 for process components and the Method 21 screening techniques are well documented. The use of Method 21 for leak detection for these components is also required under Subpart QQQ of 40 CFR Part 60, "Standards of Performance for VOC Emissions from Petroleum Refinery Wastewater Systems", as well as under Subparts K, Ka and Kb of 40 CFR 60 which involve standards of performance for storage vessels for petroleum liquids. In general, the affected components include only mechanically installed or operated components. It is assumed that the tank surface and welded seams are not affected.

Affected components on wastewater tanks, surface impoundments, containers, individual drain systems and oil-water separators, especially hatches and access doors should, for the most part, be readily and safely accessible. It is assumed, but not stated in Subpart G of the HON, that the two conditions described in Subpart H as "unsafe to screen" and "inaccessible" will also apply to Subpart G affected components. This would eliminate the need to use method 21 for such applications as insulated tanks and tank roofs where components cannot be reached safely.

3.3.2 GROUP 1 AND GROUP 2 CLASSIFICATION

Within the HON, the classification of an existing storage tank as group 1 (requiring control) or group 2 (not requiring control) is dependent on the size of the storage tank and the HAP vapor pressure. Table 5 of Subpart G is reproduced in Table 3.1.

Table 3.1: GROUP 1 STORAGE VESSELS AT EXISTING SOURCES

Vessel Capacity (m ³)	Vapor Pressure ^a
75 < capacity < 151	> 13.1
151 < capacity	> 5.2

^a Maximum true vapor pressure of total organic HAP at storage temperature

A fixed roof alone is acceptable control technology for group 2 storage vessels.

Within the wastewater provisions, the classification of a vessel as either group 1 or group 2 is dependent on whether the vessel receives any group 1 wastewater. The partial pressure of the HAPs within the vessel is not considered. Thus, there is the potential for many wastewater vessels to be classified as group 1 although they would be classified as group 2 if they were storage vessels. A hypothetical example for a wastewater tank receiving a single stream with a benzene concentration of 1000 (mg/L) is presented in Table 3.2. Since the mass emission rate of HAPs from vessels is dependent on the partial pressure of the HAPs in the vapor, the group 1 and group 2 definitions within the wastewater provisions will, in some cases, result in considerable expense with marginal reductions in HAP emissions. Application of the definition for storage vessels would reduce the cost in these cases. In cases where establishing the total HAP partial pressure may be difficult, because of a highly mixed matrix or highly variable concentrations, the present definitions within the wastewater provisions can be applied.

The applicability of Method 21, with a leak definition of 500 ppmV, for detecting leaks from wastewater tanks storing low and moderate concentration wastewaters is also questionable. While it is feasible for a wastewater with a high VOHAP content to produce a vapor content of greater than 500 ppmv in a fixed roof vessel, it is conceivable that low concentration wastewater would produce a vapor content much less than the 500 ppmv leak definition. Therefore, using Method 21 with a leak definition of 500 ppmv in these cases would not result in the detection of leaks, and the conduct of the Method 21 leak detection program would be futile. If operators were allowed to be excused from the application of Method 21, if they establish that it would not detect leaks because of the low concentration of the wastewater, needless expenses would be reduced.

3.3.3 TEST PROCEDURE

Under the equipment leak provisions, it is assumed that the process components are always under positive pressure if in service, and therefore can be leak checked at any time. However, under the wastewater provisions, no definition of conditions under which the tanks must be leak checked is provided. Fixed roof wastewater tanks can be under positive pressure when being filled, but may be under negative pressure when being emptied, or when vapors are being drawn to the closed vent system and control device. When the vapors within a fixed roof tank are under negative pressure, no leaks can occur and Method 21 screening will not produce meaningful results. Therefore, it is recommended that the measurement of static pressure within a fixed roof system be incorporated into the definition of applicability of Method 21 for leak detection. The use of Method 21 would thus be precluded for tanks under a continuous negative pressure.

3.3.4 INSTRUMENT CALIBRATION AND RESPONSE FACTORS

Within Method 21, response factor is defined as the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation. Section 63.145(e) of Subpart G describes how Method 21 will be used to determine compliance for leak detection in wastewater tanks, surface impoundments, containers, individual drain systems and oil-water separators. Section 63.145(e)(4) describes the calibration levels of the Method 21 detector and states that the calibration gas will be a mixture of methane in air. This restriction to the use of methane as the calibrant gas restricts the provisions of Method 21 which allows the use of several reference gases for which response factors of the affected VOHAP have been determined and/or have been published. In fact, limiting the calibration gases to methane in air also limits Method 21 to the use of an instrument with an FID or NDIR detector because a PID will not respond to methane. This presents a problem for those VOHAP compounds for which the PID has the optimum response.

Section 63.145(e)(7) describes how a response factor will be determined for each Group 1 wastewater stream. In a typical Method 21 application, the process stream most often contains only one volatile organic compound, and the response factor for that particular compound is used. For Group 1 wastewater streams, the generated vapor may contain a number of VOHAP compounds, and may be highly variable. Section 63.145(e)(7) states that the response factors used will be the instrument response factor at the 500 ppm level for the VOHAP present at the highest percentage in the process stream. The chemical composition of the wastewater stream is used to determine the predominant VOHAP. Chemical composition of individual process streams may be determined by sampling, engineering calculations, or process knowledge.

Using the predominant VOHAP in the wastewater stream to determine the Method 21 response factor could present some problems. For instance, if the predominant VOHAP has a poor response, and therefore a large response factor, and there is a secondary VOHAP present at a lower concentration but has a good response factor, the screening values obtained could be biased high. Also, depending on such properties as volatility, boiling point

732 15th Ave
Seattle, WA 98122
October 22, 1990

William K. Reilly
EPA Administrator
Washington, DC 20460

Dear Mr. Reilly:

As concerned and informed citizens,
we are writing to urge you to reject
the Ethyl Corporation's application to use
MMT as a gasoline additive.

We feel that the potential hazards to
health and the environment far outweigh
any benefits of this practice.

Thank you

Sincerely,

Almeta VanReth MD
John Mueller MD

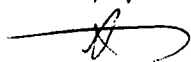
10/30/90

Dear Administrator Reilly,

I'm ~~am~~ writing a brief note to you, on behalf of the Environmental Defense Fund, to ask that you not allow Ethyl corporation to release their product "HiTEC 3000." I do not believe releasing manganese into our air is a prudent thing to do.

There is no need to acknowledge this letter.

Thank you



Steve Shapiro

Po Box 27630

Houston TX 77227-7630

11:53

Shanti Shanti Kaur Khalsa
P.O. Box 35882
Los Angeles, CA 90035

William Reilly, Administrator
Environmental Protection Agency
401 M Street SW
Washington, D.C. 20460

Dear Mr. Reilly,

Ethyl Corporation's application to the EPA for approval of "HiTec 3000" should be denied. This new gasoline additive, touted by Ethyl as "environmentally safe," contains manganese, a toxic heavy metal known to produce symptoms of Parkinson's disease at high doses. Adding "HiTec 3000" to gasoline will release into the environment large amounts of manganese, whose long-term effects on human health are unknown.

Ethyl Corporation's last experimental exposure of the entire population of our nation to a toxic heavy metal began in 1925, when they were the first to champion the use of lead additives in gasoline. Leaded gas has, in the last 65 years, been a major contributing cause of chronic lead poisoning in millions of children around the world.

Ethyl must not be allowed to conduct another such experiment as they reap great profits in the name of helping the environment! I strongly urge that you deny Ethyl Corporation's application for "HiTec 3000."

Most sincerely,

Shanti Shanti K. Khalsa

Shanti Shanti Kaur Khalsa

and vapor pressure, the predominant VOHAP in the wastewater stream may not necessarily be the predominant VOHAP in the vapor stream.

4 DISCUSSION OF METHOD 304

4.1 BIOLOGICAL WASTEWATER TREATMENT

Most SOCMI facilities employ the activated sludge process, or a variation of it, for treatment of their wastewaters. In the activated sludge process, a mixed culture of microorganisms is brought into contact with wastewater under aerobic conditions for six hours or greater. The required oxygen is generally supplied by mechanical surface aerators or by diffusing air from the bottom of the aeration tank to the surface. In the aeration tank, biodegradable organics are assimilated by the microorganisms, producing biodegradation products and additional biomass. The aeration tank effluent proceeds to a clarifier where the biomass is separated from the treated liquor by gravity sedimentation. The clarifier overflow proceeds either to further treatment or discharge. The concentrated biomass underflow is returned to the aeration basins to maintain an appropriate microbial population. Biomass is continuously removed from the system to balance the growth of biomass. This biomass is referred to as waste sludge and is directed to further treatment. Organics which sorb onto the sludge, and are not biodegraded, are removed from the wastewater stream with the waste sludge. Some plants regularly add activated carbon or other sorbents to the aeration basin to enhance the removal of organics by sorption.

4.1.1 FATE MODELS

Within the activated sludge process there are three potential removal mechanisms of organic compounds:

- stripping and volatilization
- sorption and removal with waste sludge
- biodegradation

A considerable quantity of oxygen must be continuously supplied to the aeration basin to maintain aerobic conditions. Organic compounds will transfer from the liquid to the air phase during this aeration period. They will also transfer to the atmosphere through surface volatilization which is enhanced by turbulent conditions that occur at drops and flumes. The rate of removal of a compounds by stripping and volatilization depends on the volatility of the compound and the plant operating conditions. Volatilization losses can be minimized by installing high efficiency aeration devices and reducing turbulence, or installing covers³.

All organic compounds sorb onto biomass to some degree. The tendency to sorb onto biomass is a function of the chemical characteristics of the compound. Physical sorbents, such as activated carbon, can be regularly added to the biomass in the aeration basin, increasing the tendency for sorption. As biomass is continuously wasted from the aeration basin, sorbed organics are simultaneously removed. Thus, the rate of removal of organics by sorption is a function of the biomass wasting rate and the tendency of the organics to sorb to the sludge.

In biodegradation, the compounds are oxidized by the biomass into metabolite

compounds or converted into cell mass. With complete biodegradation, the original compound and the resulting metabolites are completely converted into either CO_2 or biomass. The rate of removal of the parent compound is generally referred to as the biodegradation rate for the compound. The biodegradation rate is a function of the chemical characteristics of the compound and the process operating conditions. Compounds that are removed rapidly under a variety of operating conditions are referred to as biodegradable. Compounds that are removed more slowly or not at all are referred to as recalcitrant. However, the biodegradation rate for a compound can increase dramatically as the biomass becomes acclimated to its presence. The time for acclimation to occur may range from minutes to weeks. The presence of one compound may also enhance or inhibit the biodegradation rate of other compounds.

Within a given activated sludge system, the three removal mechanisms are independent although they compete with each other. That is, under steady state conditions:

$$\text{Overall Removal} = \text{Biodegradation} + \text{Stripping/Volatilization} + \text{Sorption}$$

If the rate of biodegradation is very rapid, the total removal by the other two mechanisms will be small. If the removal rate of all mechanisms is low, the overall removal will be small and the compound will appear in the effluent at concentrations near the influent concentration.

The rates of removal by volatilization/stripping and sorption onto waste activated sludge can be quantified to a reasonable degree of accuracy because they are based on physical-chemical characteristics and physical mechanisms that are reasonably well understood. Factors influencing the biodegradation rate of a specific contaminant include the concentration of the contaminant, the concentration of biomass, the presence or absence of other compounds, nutrients, type of microorganisms in the biomass consortium and their prior exposure (or lack of) to the contaminant of interest. The actual biodegradation rate of a compound may continuously change with time. However, general tendencies for a compound to biodegrade or not are a function of chemical characteristics (e.g., degree of chlorination, molecular structure). Thus biodegradation kinetic constants from data-bases can be used as a starting point for predicting biodegradation rates.

4.2 REGULATING BIOLOGICAL TREATMENT UNITS FOR HAP EMISSIONS

Many of the HAPs considered in the HON are readily biodegradable and biological treatment is potentially a very effective method for treatment. However compounds will be biodegraded to varying extent depending upon the factors previously defined. The HON regulation requires demonstration of specified levels of destruction for HAP compounds and that predictive models can be employed for this purpose. These models have been developed for estimating the fate and removal of organic compounds by the three potential removal mechanisms. Examples of these models include WATER7, PAVE and TOXCHEM. The individual models must be configured to represent the physical characteristics of the treatment plant. For example the physical dimensions, hydraulic characteristics of the aeration basin, the aeration rates, etc. must be accurately established and input to the model. Secondly, the physical-chemical characteristics of the compounds of interest must be input

for predicting removal by stripping/volatilization and sorption. These parameters include Henry's law coefficients and octanol-water partition coefficients. Finally, the biodegradation rate coefficient for the individual compound must be input into the model. The proposed method for obtaining site-specific biodegradation rate coefficients for HAP compounds is method 304.

4.3 METHOD 304 PRINCIPLE

A self contained benchtop bioreactor system, simulating the activated sludge process, is assembled in the laboratory. A sample of mixed liquor is added and the waste stream is then fed continuously. Oxygen is supplied to the biomass by diffusing air, supplemented with oxygen, through the aeration tank. The air is continuously recycled through the air tight system minimizing losses of organics by stripping/volatilization. The reactor is controlled to simulate the operating conditions of the full scale plant such as hydraulic residence time and MLSS concentration. Following the achievement of steady state conditions, samples of the influent and effluent wastewater are taken and analyzed for the compounds of interest. Since stripping and volatilization losses have been minimized, the rate of biodegradation of a specific HAP is calculated by the difference between the influent and effluent sample concentrations.

4.4 CONCERNS WITH METHOD 304

Introduction

This section of the report deals with a critical assessment of Method 304 contained in the HON. This method is intended to provide accurate estimates of biodegradation rate coefficients that would subsequently be employed in models for predicting destruction and emissions to the atmosphere of HAP compounds. Fundamentally, the test is valid for determining first order biodegradation kinetics in the experimental system. However, the procedure is complex, and may not provide the appropriate bio-kinetic constants for application of the model to the actual treatment plant. These concerns with the method and its application are presented in the following sections.

Operational Concerns

The determination of biological rate coefficients has been, and continues to be, the subject of significant research effort. Many measurement techniques have been used, although a universal standard method has not been accepted. The degree of biological degradation is dependent on site specific circumstances - the environmental matrix, microbial concentration and status (pure or mixed microbial culture), degree of acclimation, substrate concentration and status (single or mixed) and the environmental conditions of the test. It is difficult to define appropriate test conditions that address all applications. In this case, a method is required to satisfy the U.S. EPA that SOCM1 sector members can satisfactorily measure biological degradation rate coefficients simultaneously for a range of HAPs specific to their facilities and for mixed microbial cultures specific to their plants.

The proposed method 304 is complex and will require skilled personnel to implement. It will likely take weeks or months to measure the coefficients and therefore, be costly. The method does not use the modern method of establishing biological equilibrium (SRT control) relying, instead, on the traditional method of controlling mixed liquor suspended solids concentration. The method does not lend itself to activated carbon assisted activated sludge systems. It does not take account of removal by sorption. The selection of materials of construction are inappropriate in some cases. The desired standard of accuracy is unrealistic given the nature of the substrates. In summary, the proposed method is significantly flawed and requires improvement to ensure that the industry will provide the U.S. EPA with accurate and meaningful data. Concerns have been summarized in three categories, system design, system operation and sampling and analysis.

Reactor Design

The reactor volume may be insufficient to accommodate analytical sample volume requirements at the long hydraulic retention times utilized by some plants. The sealed flange structure allows no access to submerged instruments for removal of slime accumulations. The practice of venting defeats the purpose of the complex gas recirculation system in eliminating volatilization.

Presumably the level of gas recirculation must be high, since at the normal levels of mixed liquor suspended solids concentration carried in laboratory simulations of industrial activated sludge systems, aeration alone is not usually sufficient to suspend the biomass. Mechanical stirrers are a normal part of this equipment.

There is the potential for a build-up of volatile compounds (not necessarily HAPs) within the aeration section because of the continuous gas recycle. These compounds may be inhibitory to the biodegradation of the HAPs and cause lower biodegradation rate constant to be measured that would occur at full scale.

In experiments conducted at the Research Triangle Institute⁴, it was identified that the tubing used in the peristaltic pumps was silicone. This is unsuitable for some VOCs since they can diffuse through the silicone while under pressure from the pump rollers. Viton is the normally accepted tubing used in this type of work.

Given that industrial wastewaters tend to foam, a considerable resistance to airflow can be developed at the water - air interface. Given that the system is sealed, the role of the syphon breaker is critical in preventing blowout of the clarifier contents by the recirculating gas. The sealed nature of the clarifier prevents any maintenance. Slime will grow on the walls of the clarifier and needs to be removed since it will impact the kinetics of organics removal.

Growth of biomass on the bioreactor walls will almost certainly occur. This will not be measured by the suspended solids tests. Hence, biodegradation rates which are estimated on the basis of volatile suspended solids concentrations will be higher than the actual values.

It is not obvious how the liquid level is maintained in the aeration basin. If a standpipe

is employed, the liquid level will fluctuate with any pressure build-up or vacuum created in the headspace.

These types of investigations are generally carried out in fume hoods which lend themselves to easy temperature control using a thermostatically controlled air blower. This may be considered to be a lesser safety hazard than the immersion heater.

It is not easy to control dissolved oxygen (DO) to the specified accuracies at laboratory scale. The requirement to control DO to within 0.5 mg/L is unrealistic when the DO in full scale reactors can vary from 1 to 6 mg/L in a day.

The use of a pure oxygen atmosphere in the reactor presents a potential for explosion hazards with some of the compounds present in SOCMI wastewaters. The method specifies that the headspace gases should be closely monitored if explosive gases are expected. However, no guidance is provided for this monitoring. The method should specify the type of equipment, how it will be employed and how frequently the headspace should be monitored. As well, the remedial actions to be taken if there is an accumulation of explosive gases should be specified. It is not certain that this system can be operated safely under all conditions.

The specified equipment is presently not commercially available. It is estimated that the cost for customized construction would be approximately \$10,000. Fume hoods and refrigerators which must be dedicated to the reactor operation have not been included in this cost estimate.

System Operation

It is highly unusual to store wastewaters containing priority pollutants in polyethylene containers because of the propensity of some organics to sorb to the container walls. Storage should be in teflon, glass or stainless steel containers.

It is evident from the proposed maintenance schedules that SRT (solids retention time) is not contemplated as a control strategy. This is inadequate since there is no positive control over microbial growth rate. With the complex organics present in SOCMI wastewaters, it is imperative to retain the biomass in the system as long as is required to promote the slow growing organisms that can degrade these organics. The proposed strategy of mixed liquor suspended solids concentration control is inadequate.

The headspace composition at initiation of the test is important in maintaining a particular dissolved oxygen concentration during the test. It will be very difficult to maintain a set dissolved oxygen concentration without a pressure or vacuum build-up in the aeration basin headspace. In experiments conducted at Research Triangle Institute⁴, the DO concentration trended below the designated experimental conditions. In this case aeration gas was bled from the system creating a vacuum which triggered the pressure sensitive relay to open a solenoid valve and admit oxygen to the system.

It seems an extravagant requirement to discard tubing once it is blocked. Most laboratories would clean out the tubing and use it again. The target of 5% flow variability is also hard to achieve under laboratory scale conditions. A target of 10% flow variability is a more practical recommendation.

It is not clear what is meant by "the targeted conditions" with respect to attaining steady state? Is this meant to be biological steady state? If so, how is this to be measured? If not, what are the conditions of concern? To achieve biological steady state will require operation for several solids retention times.

Foaming is an operational problem experienced with industrial wastewaters and is normally mitigated through the use of defoaming agents. Sometimes the defoaming agents have an inhibitory effect on the biomass especially if nitrification is required. A concern is that defoamers may be required in a bench scale system when it is not being employed in the full scale system. Guidance is required for this eventuality.

A constant feed from a full scale equalization tank is presented as an alternative for wastewater supply to the process units. Contaminant concentrations in equalization basins can fluctuate substantially, thereby negating the steady state assumptions on which the technique is based.

The technique assumes that the dissolved concentration of the contaminants is equal to the effluent concentration. However, given the presence of biosolids in the clarifier overflow, sorbed chemical will also exit the clarifier. For some compounds which tend to sorb to greater extent, this will result in an underestimation of the biodegradation rate constants as the measured effluent concentration will be higher than the actual soluble concentration of contaminants.

It is estimated that the reactor may need to be operated for at least 2 weeks to meet the stated objectives. This is based upon a Hydraulic Retention Time (HRT) of 24 hours and a scenario where:

- Steady state is attained in 2.5 days
- 6 samples are taken over the next 2.5 days
- Laboratory analyses requires 3 days
- 15% RSD criteria is not met
- 4 more samples are taken over next 2 days
- Laboratory analyses requires 3 days
- 15% RSD criteria are met

Assuming that a technician will, on average, devote 4 hours per day to the test and a charge out rate of \$75/hour, operation of the reactor will cost \$4200.

Assuming that to meet the requirement of 15% RSD, 10 samples of the influent and effluent are required and that VOC and extractable compounds are to be analyzed in each sample by an external analytical laboratory, sample analyses will require \$15,000 per run.

This assumes a total cost of both analyses for each sample of \$750.

If biomass from an operating plant is employed for a test with wastewater and with operating conditions similar to that of the full scale plant which it has been previously exposed, then acclimation should not be an issue. If a different biomass is employed then the method will have to be operated for 2 to 3 solids retention times to allow for acclimation. This would serve to further extend the length and cost of an experimental run.

Sampling and Analysis

The requirement that the influent and effluent measurements have a Relative Standard Deviation (RSD) less than 15% requires that sample analysis be completed during the experimental run. Assuming 6 samples, with 8 hour intervals between samples, only 48 hours is allowed for all of the sample analysis. This is quite unrealistic unless a fully equipped analytical laboratory is dedicated to the experiment. It is our experience that samples of this nature could not be turned around in less than a week.

A required RSD of less than 15% is unrealistic when analyzing contaminants at relatively trace concentrations in the complex matrices under consideration. It is unlikely that even split samples could regularly achieve this level of precision.

Some of the HAP compounds can not be analyzed by the standard VOC analysis. Examples include acetaldehyde, 2,4-dinitrophenol, 2,4-dinitrotoluene, methanol and naphthalene. It is possible that as many as 4 separate analyses may be required for a sample from a given wastewater stream. This will add significantly to the cost of a test. In addition, much greater sample volumes are required than the specified 40 ml amber vials. It may be that as much as 2.0 L of sample might be required. For long HRT systems, with low flow rates, this volume of sample may be difficult to obtain.

Application of Method Results

The method presents a technique to calculate first order biodegradation rate constants and, given steady state operation at only one operating condition, this is all that can be calculated. The CHEMDAT and WATER7 models which are specified in Subpart G employ Monod kinetics for biodegradation rates and these can not be obtained with the information acquired by the prescribed technique. The appropriate kinetic constants can be obtained with multiple experiments, but this will increase test costs considerably.

The regulation requires that the test must be repeated if the full scale wastewater treatment plant operating conditions are changed. The method must define what constitutes a change that is significant enough to require a repeat of the method.

Models may be employed if their predictions are consistent with the observed effluent concentrations in the full scale wastewater treatment plant. The level of consistency and statistical techniques employed for this analysis should be specified. For example a model requires plant data as input. This input will have variability associated with it and therefore

guidance is required as to which values should be employed (arithmetic mean, geometric mean, log-mean, median, etc). Once the input data have been selected the model will output a single value for the effluent concentration. This value will need to be compared against the data collected on the plant effluent concentrations. The number of effluent concentrations required, how they are to be collected, and the statistical tests required to compare the model predictions with the measured data need to be specified.

The regulation does not specify action to be taken if the model which has been calibrated by Method 304 does not accurately predict the effluent concentrations of the full scale plant.

4.5 ALTERNATIVES TO PROPOSED METHOD 304

As described in the prior section, proposed Method 304 will be complex to perform on a frequent basis as required for compliance demonstration. Therefore, two alternative methods are proposed by which biodegradation of HAP compounds in SOCMI wastewater treatment plants can be estimated. In the first approach, an alternative bench scale technique for estimating biodegradation rate constants is proposed. In the second approach, measurement of the contaminant behaviour in the full scale plant is employed along with a model to estimate the fraction of contaminants biodegraded.

4.5.1 ALTERNATIVE BENCH SCALE DETERMINATION OF BIODEGRADATION RATE CONSTANTS

A possible alternative method for obtaining biodegradation rates is to employ an open bench scale system where the emissions of contaminants in the offgas are measured and quantified as a mass flux. This mass flux is then considered when biodegradation rate constants are calculated. This method has the advantage of simplicity of operation with more conventionally available equipment. As well, two sets of response data are obtained which will yield more information than the technique specified in Method 304. This is especially important for compounds which are removed to below the liquid phase detection limits. Aeration basin concentrations can be estimated from measured gas phase concentrations that can generally be detected with more sensitivity. A disadvantage of the proposed technique is that a number of gas phase sampling procedures and analyses may be required to quantify the offgas emissions. Development work might be required to perform gas phase sampling and analysis for some of the compounds on the SOCMI HAP list. This, however, may still be preferable to trying to perform Method 304 as it is presently proposed.

4.5.2 FULL SCALE CALIBRATION

Method 304 is required because it is assumed that the biodegradation rate coefficients are the most difficult to ascertain. The results from this test are intended to be employed in models such as WATER7 where stripping/volatilization, sorption and destruction by biodegradation are estimated. It is therefore assumed that the stripping/volatilization and sorption models are correctly formulated and calibrated. If this is the case, then calibration of the biodegradation rate coefficient to match the predicted effluent concentration with that

observed at full scale is valid. The calibrated model will estimate the contribution of all four mechanisms competitively. This approach has been successfully employed to aid in obtaining permitting for a POTW expansion at the Seattle Renton plant⁵. This approach works for chemicals present in existing wastewater treatment plants. Another approach must be employed if approval of new chemicals is required a priori, however, Method 304 is not valid in this case either.

4.5.2.1 FULL SCALE CALIBRATION WITH MULTIPLE SAMPLING LOCATIONS

The degree of uncertainty that is associated with using full scale plant data can be reduced by sampling all process transfer streams in the wastewater treatment plants. For processes where biodegradation is minimal (e.g. clarifiers, neutralization) then losses between influent and effluent may be attributed to volatilization, and adsorption. Biodegradation in aeration basins can be determined by measuring the influent and effluent concentrations estimating the mass flow removed by sorption and stripping/volatilization with appropriate models and attributing any other mass lost in the aeration basin to biodegradation.

For example, for a simple completely mixed system, at steady state, the mass balance equation is:

$$Q(C_i - C_o) - r_s - r_b = 0$$

where:

Q = wastewater flow rate

C_i = influent wastewater concentration

C_o = effluent wastewater concentration

r_s = and volatilization rate

r_b = biodegradation rate

Values of the influent and effluent concentration are measured in this approach, r_s is estimated using the appropriate models and the only unknown is r_b , which can be estimated. The fraction of the contaminant destroyed is therefore equal to:

$$\text{Fraction Destroyed} = \frac{Vr_b}{QC_{i,plant}}$$

where:

$C_{i,plant}$ = Concentration in wastewater entering treatment facility

The costs associated with analysis of samples taken at numerous locations must be acknowledged.

5. DISCUSSION OF METHOD 305

5.1 METHOD PRINCIPLE

Method 305 is a combination of method 25D for the measurement of total VO in wastewater and Method 18 for speciation of individual HAPs. In Method 25D, wastewater samples are drawn from taps on the wastewater stream line, through a static mixer and cooling coil, into prechilled polyethylene glycol (PEG). The sample in the PEG is added to water in a special purge chamber, heated to 75 °C and purged for 30 minutes at a flowrate of 6 L/min. The purge gas is split and passed continuously through a flame ionization detector and a Hall detector. The total response of the two detectors integrated over 30 minutes are compared to the total responses for known amounts of two representative compounds.

Method 305 differs from Method 25D in the analysis and quantification of the purge stream. In Method 305, the purge gas passes over a sorbent tube to collect volatile organics. The sorbent tube is either solvent-desorbed or thermally desorbed for analysis by gas chromatography with an appropriate detector. Individual HAPs recovered from the sorbent tubes are quantified against standards of the same compounds analyzed on the gas chromatograph. Results are corrected for recovery efficiency as determined in a separate experiment by spiking known amounts of the compounds into the gas stream immediately upstream of the sorbent tube. Total VOHAP concentration is calculated by summing the mass of all individually speciated HAPs collected on the sorbent tube and dividing the sum by the wastewater sample volume.

5.2 CONCERNS WITH METHOD 305

5.2.1 GENERAL APPLICABILITY

The elevated temperature (75 °C) and purging length do not represent the volatilization and stripping conditions generally encountered during wastewater collection and treatment. In addition, the addition of PEG provides a matrix not typical of wastewater streams. Thus, the concentrations measured by Method 305 do not relate to expected emissions during wastewater collection and treatment. Thus the classification of a wastewater as either group 1 or group 2 is based on an arbitrary measurement of concentration.

Classical EPA approved analytical techniques have been used for years to comply with NPDES and other water pollution regulations. There is no need to require development of additional data or to further document data quality from these methods. Since the measurement is arbitrary in the first place, direct measurement of the contaminants in the wastewater streams for the limited number of compounds on this list by these methods is preferable to the indirect, unproven technologies proposed in Method 305. If a gas phase measurement is required, headspace GC, in which equilibrium between the liquid and gas phases is used rather than purging is a potentially simpler alternative.

5.2.2 SAMPLING PROCEDURES

Method 305 requires the use of procedures specified in Method 25D for sample collection. The samples are collected into a pre-weighed, chilled vial containing polyethylene glycol. The sample is drawn from a tap on the waste line, passed through a static mixer and cooling coil and then introduced into the sample vial below the level of the PEG. The wastewater is chilled before exiting the line and never exposed to ambient air, thus minimizing the potential for losses of volatile components. The vial is filled and capped with minimum headspace. No holding time limits are specified by the method. While, the specified sampling technique in Method 25D should minimize losses by volatilization, losses into headspace in the PEG vial may occur. To our knowledge, studies to monitor losses of volatiles from PEG over time have not been published, and data for samples with extended holding times would be potentially compromised.

Routine EPA Methods (such as Method 8240 of SW-846 or Federal Register Method 624, or the EPA Contract Laboratory Statement of Work) for the analysis of wastewater for volatile organics require collection of the sample into a vial with capping such that no headspace is present. These methods do not address wastewater stream specific requirements such as separate sampling line taps with static mixers and cooling elements. Samples are chilled after collection to minimize volatilization losses and they may be preserved against biodegradation with hydrochloric acid. Method holding times of 7 to 14 days until analysis apply.

The sampling requirements specified in Method 25D are not insubstantial. Other EPA sampling methods are available and if operators were allowed to use them, HON implementation costs would be reduced. A change in the sampling procedure may require a modification to Method 305 in regards to sample handling in the laboratory and purge conditions.

5.2.3 EQUIPMENT AVAILABILITY

The equipment that is required for performing the analysis of samples according to Method 25D and 305 is not known to be commercially available at this time. Contact with several vendors of similar equipment have been made, to determine whether they have begun development of equipment meeting the design specifications provided in the method. None of the firms contacted indicated that they were placing significant resources towards such a program. The consensus seemed to be one of determining market potential before proceeding. There is little likelihood that a proven commercially available instrument for performing methods 25D and 305 in 1993.

There are relatively few laboratories that are currently capable of performing the analyses required by Method 305. This is due, in large part to the lack of commercially available instrumentation and the newness of the method. As a result, there is no ready source from which affected industries can procure the required services, nor is there a body of experimental data to assess the true limitations of the analytical procedures.

5.2.4 SORBENT TUBE SELECTION AND CAPACITY

The HAP list contains a range of organic chemicals. No one sorbent tube is applicable to all. Wastewater streams that contain different classes of organics, such as alcohols and chlorinated organics, would require sampling with multiple tubes. This would, in turn, necessitate either further modifications to the apparatus to split the purge stream or multiple purge sequences. Analytical costs will also be proportionally higher.

Sorbent tubes have finite capacity for organics. Most techniques which recommend their use also require measures to document the analyte losses through breakthrough. The total purge volume (180 L) of Method 305 exceeds the breakthrough volume for many sorbent tubes such as Tenax. Breakthrough is a particular concern for the use of sorbent tubes in Method 305, where the potential level of organics recovered from wastewater streams near regulatory limit may exceed some tube capacities.

The level of organics in wastewater streams, at their regulatory limit, will likely preclude thermal desorption for analysis of the sorbent tubes. For example, a 10 gram wastewater sample at the regulatory limit (10,000 ppm Subpart G Table 9 compounds) may release up to 100 mg of compound. The upper range for analysis by thermal desorption is generally under 1 mg for individual analytes.

Collection on charcoal or silica tubes for solvent desorption would pose less of a problem for breakthrough losses. The 1 gram jumbo-size tubes could be expected to accommodate emissions from high concentration wastewater streams, and the solvent extract from the tubes could be diluted to bring the concentration within instrument calibration range. However, solvent extraction has been associated with poorer precision and accuracy than thermal desorption for some of the regulated organics.

Streams from new sources which contain widely different concentration of HAPs may create severe analytical problems, since group categorization would require both that Subpart G Table 8 compounds be measured at 10 ppm and that Subpart G Table 9 compounds measured at 10,000 ppm. A Table 8 chemical present at 100 ppm in a matrix containing up to 10,000 ppm of other organics may not be detectable. High levels of any organics - HAPs or not - will compromise or preclude analyses by thermal desorption techniques. Solvent desorption analyses may also be impractical if low levels of the Table 8 compounds can not be chromatographically resolved from a much larger peak from a HAP or non-HAP compound. In the best of cases, multiple analyses will be required to quantify both Table 8 and Table 9 compounds in order to demonstrate regulatory compliance.

5.2.5 QUALITY ASSURANCE

In method 305, two tests for trapping efficiency of the purge stream and recovery of the analytes are required. The two tests are referred to as the recovery efficiency for determining trapping/desorption efficiency of individual test compounds and the correction factor for determining trapping/desorption efficiency using internal standards. However, determination of the precision of the purge step of the method is not addressed in the

method.

In method 305, recovery evaluation (RE) tests are required prior to analyses of wastewater samples. Organic-free water is added to the PEG and the heated purge cycle initiated. During the purge cycle, a spike of the HAPs expected to be present in the wastewater stream are injected into the gas stream prior to the solids sorbent that will be used to collect the HAPs from the wastewater samples. The sorbent tubes are then analyzed as they will be during the wastewater tests. The amount of organics recovered is compared to the known amount spiked. If the recovery is within 50% to 130% of the amount spiked, the sorbent tube is considered appropriate for the compounds of interest.

Method 305, as published in the Federal Register, December 31 1992 also references a correction factor (CF) and provides for its use in final calculations. However, no guidelines are provided for the determination of the factor. The earlier draft version of the method includes the internal standard procedure for determination of CF. Sorbent tubes are directly spiked with liquid solutions of representative compounds. The tubes are then analyzed as they will be during wastewater tests. The quantities recovered are compared with the quantities spiked to establish a correction factor; i.e. if a representative chemical were measured at 90% of the known amount spiked, all sample data would be adjusted upwards accordingly.

The requirements in Method 305 for either the recovery efficiency or correction factor are far less stringent than those for comparable methods using solid sorbents. Typical sorbent methods (e.g. NIOSH Method 18) require initial demonstration of precision and accuracy with a minimum of three tubes spiked at five different concentrations. The minimum acceptable recovery efficiency of 50% specified in method 305 appears arbitrary with no statistical foundation.

Method 305 specifies that the mass of an individual HAP detected on a sorbent tube be adjusted according to the following equation:

$$W_T = W_{T,d} * (1/RE) * (1/CF)$$

where:

- W_T = adjusted weight of test compound detected
- $W_{T,d}$ = weight of test compound detected on sorbent tube during test
- RE = trapping/desorption recovery efficiency
- CF = trapping/desorption correction factor

The recovery efficiency test measures losses from the purge gas through analysis. The correction factor test also measures losses through sorbent desorption and analysis. Thus, by adjusting results based on the product of the two factors, samples will be erroneously adjusted twice for the same effects.

During the sorbent desorption process, Method 305 indicates that the volume of

solvent depends on the amount of adsorbed material to be desorbed (1.0 ml per 100 mg of adsorbent material) and also on the amount of test compounds present. The method also indicates that the volume can be adjusted or diluted to bring the compound concentrations into the calibration range. If adjusted actually means concentrated, this may pose a problem with losses. In general, it is not advisable to concentrate any extract containing volatiles.

Method 305 specifies a system blank must be run daily but does not specify when it is required with regards to the number of samples analyzed. In addition, the method does not indicate an acceptable level of carryover.

Method 305 specifies analysis of three calibration standards in triplicate on a daily basis. This will require nine GC runs, or an estimated 5 hours of time just to verify the calibration. The consequence is that the number of samples that can be analyzed per day may be quite small. It is also required that all response factors be within 5% of the mean of three RFs determined at separate concentrations for a given compound. This is a strict limitation which would further reduce sample throughput.

5.2.6 INTERLABORATORY STUDY OF METHOD 25D

The purging conditions specified in proposed Method 305 are identical to those specified in Method 25D. Therefore any concerns with Method 25D would also apply to Method 305. In 1992, the EPA sponsored an interlaboratory comparison study of Method 25D using six laboratories experienced in analysis of air samples⁶. Each laboratory was provided with the required apparatus since it is not available as a commercial package. Several of the laboratories encountered difficulty in performing the method reliably, despite extensive instruction by the EPA contractor. Significant laboratory biases were found relative to theoretical values for the limited number of compounds studied. Such information indicates that further study of the test method are warranted prior to its use for regulatory compliance.

5.2.7 OPERATIONAL CONCERNS

The sample path is straightforward but is potentially quite long, increasing the chance of condensation or adsorption of analyte. The glassware would probably be difficult to clean, particularly if an extremely dirty sample is introduced or foaming occurs. It is reported that the coalescing filter can be used repeatedly without cleaning⁶. This would be a definite advantage but is unlikely always to be the case.

5.2.8 FRACTION MEASURED VALUES

Given the high costs and technical concerns for the validity of Method 305, it is likely that many SOCMI facilities will elect to use traditional wastewater analysis data and correct results with the Fraction Measured values provided in the HON for 84 compounds (Subpart G Table 13). These factors indicate the percentage of the wastewater concentration expected to be measured if Method 305 were applied. The data generally indicate 100% conversion for many of the non-polar, non water soluble compounds and lesser recoveries

for the more polar water soluble and water miscible compounds. The data for certain relatively reactive compounds, such as phosgene which has a reported F_m of 0.868, leads to concerns about data validity, since phosgene in aqueous solution reacts over time with water to form other compounds. Thus, the results obtained for phosgene must be time dependent.

The means of determination and source of these data is not described in the HON, nor have the values been widely reported in the open literature. There should be full and verifiable documentation of the procedures used and the results obtained by the EPA during the methods development process for the technique and ample time provided to permit peer review and open literature publication. The means of determination should be fully validated before factors are set in the HON.

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APPENDIX R

APPENDIX R

Emissions Averaging - Examples Illustrating Fixed Cap Approach

The use of the "fixed cap" approach is illustrated by the four example cases considered in the attached table. In these examples, the emissions average is among three points: a Group I point which is undercontrolled (debit) and two Group II points which are overcontrolled (credits). The reference control technology for the Group 1 point yields 95 per cent control. The first point is expected to emit 80 units/year uncontrolled emissions and the Group II points emit 40 units/year each. The emissions for the three points are shown for each of four quarters in a year, as well as for the full year. For each emission point, the attached table shows actual emissions if they were: uncontrolled (UNC), with averaged controls (EA), and with reference control technology (MACT). Also shown on an annual basis is the difference (Δ) between actual emissions if emission averaged controls were applied and emissions with reference control technology. The last column for each emission point (Limit/Q) shows the maximum potential emissions if reference control technology were applied.

Thus, for the "excess range" approach, the difference between EA and MACT per quarter for the Group 1 emission point (Point 1) could not be more than 125 to 135 per cent of the sum of the differences between EA and MACT for the Group 2 emission points (Points 2 and 3) for the same quarter. For the "fixed cap" approach, the difference between EA and Limit/Q for Point 1 could not be more than the sum of the differences between EA and Limit/Q for Points 2 and 3 for any quarter. Annual emission average compliance would be calculated the same way in either case.

The last set of columns shows: first, whether the annual average was in compliance (Anl Avg OK?); second, the total limit for the sum of actual emissions under the fixed cap approach for each quarter (Limit); third, the actual emission averaged emissions from all three points per quarter; and last, whether the quarterly averages were in compliance (ACT) with the "fixed cap" approach (Qrt OK?).

Four cases are outlined in the attached table to show examples of compliance and non-compliance situations using the fixed cap approach. Case 1 shows what emissions would be if Point 2 had variable emissions over the year. If a quarterly average of actuals is made for the first quarter, credits would be less than debits. (resulting in noncompliance under the excess range approach), even though the total actual emissions ($ACT = 20.75$) are less than any other quarter that year. The other quarters, when Point 2 is running at an average or higher than average rate, would have credits greater than or equal to debits. Using the fixed cap prevents this situation since ACT is less than Limit for each quarter, each quarter would be in compliance. As there were no spikes in total actual emissions (ACT), this is appropriate. For the annual average, the Δ for Point 1 cannot be greater than the

sum of the Δ 's for Points 2 and 3. Since $76 = 38 + 38$, the annual average is in compliance.

In Case II, an unanticipated variable operation of the debit generator (Point 1) resulted in 150 per cent of expected emissions for the second quarter. In that quarter, credits are less than debits and ACT is greater than Limit. The second quarter would be in noncompliance for either averaging approach; this is appropriate, as 31 units/quarter is a significant spike in actual emissions for the group of points. For the annual average, Δ for Point 1 is 76 which is equal to the sum of the Δ 's for Points 2 and 3 ($38 + 38$) -- so the annual average is in compliance.

Case III represents a situation where partial control (50 per cent) of credit generating Point 3 was in place before the base year. This would mean the credit generated from Point 3 would have to be any reduction in addition to that 50 per cent. Credits (9.5 for Point 2 + 4.5 for Point 3 = 14) would be less than debits (19) for each quarter, and the annual average would show noncompliance as $76 > 38 + 18$. While the fixed cap quarterly compliance shows compliance (ACT < Limit), this is still appropriate as the quarterly average check is to ensure significant short term spikes do not occur.

In Case IV, the debit generating unit show anticipated variable operation in the first two quarters. Both averaging strategies show noncompliance in the second quarter. Annual averaging is in compliance.

Table

GROUP 1 DEBIT							GROUP 2 CREDIT (95%)							Totals						
Point 1 = 80/yr UNC							Point 2 = 40/yr UNC					Point 3 = 40/yr UNC			Annl Avg OK?	Limit	ACT	Quart Avg OK?		
	UNC	EA	MACT	A	Limit/Q		UNC	EA	MACT	A	Limit/Q	UNC	EA	MACT	A	Limit/Q				
CASE I	1Q	20	20	1	N/A	1	5	0.25	5	N/A	15	10	0.5	10	N/A	10	-	26	20.8	X
Credit unit 50%	2Q	20	20	1	N/A	1	15	0.75	15	N/A	15	10	0.5	10	N/A	10	-	26	21.3	X
for one Q then	3Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26	21	X
150% for one Q.	4Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26	21	X
	YR	80	80	4	76	N/A	40	2	40	38	N/A	40	2	40	38	N/A	OK			OK
CASE II	1Q	10	10	0.5	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26	11	X
Debit unit 50%	2Q	30	30	1.5	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26	< 31	(NC)
for one Q then	3Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26	21	X
150% for one Q	4Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26	21	X
(not anticipated)	YR	80	80	4	76	N/A	40	2	40	38	N/A	40	2	40	38	N/A	OK			(NC)
CASE III	1Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	5/10*	-	21/26	21	X
Point 3 has	2Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	5/10	-	21/26	21	X
50% control in	3Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	5/10	-	21/26	21	X
base.	4Q	20	20	1	N/A	1	10	0.5	10	N/A	15	10	0.5	10	N/A	5/10	-	21/26	21	X
	YR	80	80	4	76	N/A	40	2	40	38	N/A	40	2	40	38	N/A	(NC)			OK
CASE IV	1Q	10	10	0.5	N/A	1.5	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26.5	11	X
Debit unit 50%	2Q	30	30	1.5	N/A	1.5	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26.5	< 31	(NC)
for one Q, 150%	3Q	20	20	1	N/A	1.5	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26.5	21	X
for one Q	4Q	20	20	1	N/A	1.5	10	0.5	10	N/A	15	10	0.5	10	N/A	10	-	26.5	21	X
(anticipated)	YR	80	80	4	76	N/A	40	2	40	38	N/A	40	2	40	38	N/A	OK			(NC)

Using the "excess range" approach to allow 125% debit/credit per quarter:

I Debit = 19; Minimum credit is in 1Q = $4.75 + 9.5 = 14.25 \Rightarrow 14.25 * (125\%) = 17.8 < 19$ (NC)

II Maximum debit is in 2Q = 28.5; Credit is 19 $\Rightarrow 19 * (125\%) = 23.75 < 28.5$ (NC)

III Debit = 19; Minimum credit = 14 $\Rightarrow 14 * (125\%) = 17.5 < 19$ (NC)

IV Same as II (NC)

APPENDIX S

APPENDIX S



ENGINEERING
P. O. Box 6090
NEWARK, DE 19714-6090

Louviers Building

March 9, 1993

Mr. Rick Colyer
OAQPS - EPA
MD 13
Research Triangle Park, NC 27711

Dear Mr. Colyer:

As I mentioned over the phone, I believe there is one step in the equipment leak regulation where several interpretation are possible. Whichever interpretation is agreed upon is probably less important than that there be a mutual understanding.

A leaking valve or flange that was repaired must be remonitored within 90 days to verify that the leak does not recur. If the leak does recur it could be 1) treated as a new leak, 2) treated as one for which the initial attempt at repair failed or, 3) put on the list for replacement at the next shutdown.

I suggest that we either 1) treat a recurrence as a new leak from a repair standpoint, but spell out in the equation for percentage leaking that only occurrence is used in the equation or 2) we define recurrence and put that equipment directly on the shutdown list.

I believe we must deal explicitly with recurrence because it has been reported to be a frequent enough phenomenon to confound the statistics for such extremely low percents leaking. For instance, the EPA Maintenance Study found about 24% recurrence leaks, at a 10,000 ppm leak definition, within 90 days of successful repair. (See attached page from Maintenance study.)


My company's experience is that field maintenance can be expected to successfully repair equipment a couple of times after which shop maintenance is required. If a valve's leak is repaired, but leaks soon, it is likely to need to be removed and worked on in the shop.

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3.5 Recurrence of Leaks

To study the recurrence of leaks after maintenance, data from the 155 attempts at maintenance were examined. Of these 155 attempts, 97 cases screened $\geq 10,000$ ppmv immediately before maintenance. For this analysis, only those valves which screened $\geq 10,000$ ppmv immediately before maintenance and screened $< 10,000$ ppmv immediately after maintenance were considered as having a potential to recur. This eliminated all but 28 valves from the analysis. Of these 28 valves, eight were seen to recur (i.e., screen $\geq 10,000$ ppmv at some time following the after-maintenance screening). Of the eight valves whose leaks recurred, four recurred within a few days after maintenance. The other four recurrences were spread over the study period (up to 7 months). Because of the two distinct groupings of recurrences over time, a mixed-model was used in estimating the recurrence rate. The exact form of the model used is described in Appendix D.

A graphical presentation of the modeled percentages for recurrence along with an approximate 95% confidence region is given in Figure 3-16. The empirical distribution function (actual data) is indicated by the dotted line.

In Table 3-7, 30-day, 90-day, and 180-day recurrence rate estimates are given along with their approximate 95% confidence limits. In comparison to occurrence rates, recurrence rates are much higher.

TABLE 3-7. VALVE LEAK RECURRENCE RATE ESTIMATES

Recurrence Rate Estimate		95% Confidence Limits on the Recurrence Rate Estimate
30-day	17.2%	(5, 37)
90-day	23.9%	(7, 48)
180-day	32.9%	(10, 61)

APPENDIX T

APPENDIX T

Table 9 Strippability Groups

[illegible]

* GC method which cannot absolutely identify an analyte. Recommended only for "clean" samples or those for which the "600 Series" Methods: Clean Water Act

^{oo} New proposed method. MDL depends on chromatographic column selection.

*** HPLC method which cannot absolutely identify an analyte.

The first value denotes an MDL (usually a Drinking Water Method) currently attainable in some commercial lab.

The second votes indicated an MDL that in proposed QC methods A/or and could only be used to demonstrate that the concentration of the substance in the sample was not greater than the MDL. ND - no MDL given.

"8000 Series" Methods: SW-846 3rd Edition Revisions 0-2 (RCRA)

"500 Series" Methods: Safe Drinking Water Act

CLP Methods OLM01.0-7: EPA Central Laboratory Program-CERCLA (Superfund)

ND - no MDL given

NOTE: Summary MDL column does not MDLs attainable on pristine water

HAZARDOUS ORGANIC NESHP

Table 9 Strippability Groups			
		Summary	
Group	Chemical Name	CAS No.	MDL, ug/L
A	Biphenyl	92524	no EPA method other than 25D
A	Butadiene-1,3	106990	no EPA method other than 25D
A	Ethylene oxide	75218	no EPA method other than 25D
A	Hexane	110543	no EPA method other than 25D
A	Methyl tert butyl ether (MTBE)	1634044	no EPA method other than 25D
A	Nitropropane	79469	no EPA method other than 25D
A	Phosgene	75445	no EPA method other than 25D
A	Propylene Oxide	75569	no EPA method other than 25D
A	Triethylamine	121448	no EPA method other than 25D
A	Trimethylpentane, 2,2,4-	540841	no EPA method other than 25D
A	Vinyl acetate	108054	no EPA method other than 25D
B	Chloroacetophenone-2	532274	no EPA method other than 25D
B	Dimethylaniline-N, N (N, N Diethylaniline)	121697	no EPA method other than 25D
B	Ethyl acrylate	140885	no EPA method other than 25D
B	Ethylene glycol dimethyl ether	110714	no EPA method other than 25D
B	Ethylene glycol monobutyl ether acetate	112072	no EPA method other than 25D
B	Propionaldehyde	123386	no EPA method other than 25D
C	Aniline	62533	no EPA method other than 25D
C	Dimethyl hydrazine-1,1	57147	no EPA method other than 25D
C	Dimethyl sulfate	77781	no EPA method other than 25D
C	Dioxane-1,4(1,4-Diethyleneoxide)	123911	no EPA method other than 25D
C	Epichlorohydrin(1-Chloro-2,3- epoxypropane)	106898	no EPA method other than 25D
C	Ethylene glycol monomethyl ether acetate	110496	no EPA method other than 25D
C	Diethylene glycol diethyl ether	112367	no EPA method other than 25D
C	Diethylene glycol dimethyl ether	111966	no EPA method other than 25D
C	Ethylene glycol monoethyl ether acetate	111159	no EPA method other than 25D
C	Methanol	67561	no EPA method other than 25D
C	o-Toluidine	95534	no EPA method other than 25D